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Preparation of Intrinsic Plutonium Colloids by Sonolysis of PuO₂ in Water

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INTRODUCTION

Colloidal species of Pu(IV) were shown to play a central role in the speciation of plutonium in various aqueous wastes and in biosphere [1-3]. However, a comprehensive understanding of the behavior of Pu colloids remains elusive and hinders progress on the development of reliable processes of their management. Preparation of plutonium colloidal species with controlled composition and properties is still a challenge. Usually, the intrinsic Pu(IV) colloids are composed of highly charged polynuclear species containing significant amounts of coordinated anions originated from electrolyte salts [2,4,5]. Herein, we report the preparation of stable Pu(IV) colloids by the action of ultrasonic waves on PuO₂ in pure water without any salts or stabilizing reagents.

DESCRIPTION OF THE ACTUAL WORK

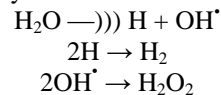
Ultrasonic treatment of PuO₂ calcined at 600°C has been performed using 20 kHz ultrasound at the acoustic power of 0.34W·mL⁻¹ (measured by thermal probe method) in pure water saturated with argon, Ar/10%CO or Ar/20%O₂ gas mixtures. Temperature of 25°C inside the sonoreactor during sonolysis was controlled by a cryostat. The reactor was installed in the hot glove box at ATALANTE research facility. Some of Pu(IV) colloids were prepared by the dilution of concentrated Pu(IV) nitric solutions in water. The obtained colloids have been characterized by UV/Vis and XAFS spectroscopy. XAFS measurements (Pu L3 XANES and EXAFS, fluorescence mode) have been performed at ROBL beamline (ESRF Grenoble). STXM measurements have been performed at LBNL ALS-MES Beamline (E = 800.013 eV).

RESULTS

The 5 h sonolysis of a PuO₂ suspension in pure water under Ar bubbling leads to the formation of a green colloid solution ([Pu]~1.5·10⁻³ M) which remains stable for months after the removal of big PuO₂ particles by centrifugation at 9000 rpm (Inset of Fig. 1). The concentration of Pu in colloidal solution is increased approximately linearly with time of ultrasonic treatment.

The mechanism of Pu colloids formation in studied system is an intriguing question. It is well known that the application of ultrasound in heterogeneous systems

enhances erosion, fracture, and dispersion of solids [6]. However, the same experiment performed with ThO₂ as a model of PuO₂ does not lead to the formation of colloids. Therefore, the mechanical effects of ultrasound cannot explain colloids formation. Consequently, a chemical reactions between PuO₂ and sonochemically generated chemical species should be taken into account. Acoustic cavitation causes the homolytic splitting of water molecules followed by the formation of H₂ and H₂O₂:



where the symbol "ultrasound" indicates a plasmochemical process inside the cavitation bubbles [7]. In the presence of oxygen the yield of H₂ is sharply decreased and the yield of H₂O₂ is raised due to the scavenging of H atoms [8]:

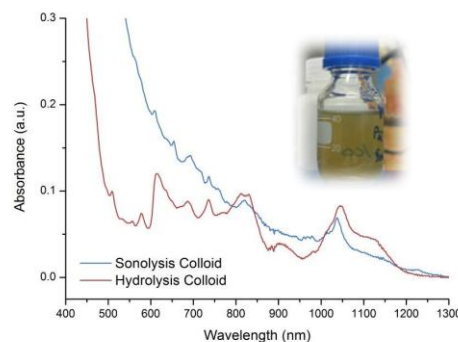
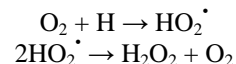
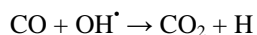


Fig. 1. The Vis/NIR spectra of Pu colloids obtained by PuO₂ sonolysis (pH~6) and Pu(IV) hydrolysis (pH~2.5), [Pu]= (7-9)·10⁻³ M, l= 1 cm. Inset – photograph of sonochemical Pu colloidal solution after centrifugation at 9000 rpm.

Interestingly, the sonolysis of PuO₂ in the presence of Ar/20%O₂ gas mixture does not lead to any formation of Pu colloids. By contrast, the rate of Pu colloids formation was found to be increased in the presence of Ar/10%CO gas mixture compared to pure Ar. Carbon monoxide plays a role of OH[•] radicals scavenger providing a higher yield of H₂ [9]:



Therefore, it can be concluded that the mechanism of Pu colloids formation consists of Pu(IV) reduction by hydrogen produced during water sonolysis. Then, Pu(III) soluble species are re-oxidized to Pu(IV) yielding colloids. Most probably, Pu(IV) reduction occurs due to the local transient heating generated by cavitation bubble collapse [6]. Presumably, Pu(III) is oxidized in solution by OH^{\cdot} radicals and/or by H_2O_2 .

Fig. 1 shows the Vis-NIR spectra of Pu colloids prepared by sonolysis and by hydrolysis of Pu(IV). The spectra of hydrolyzed Pu(IV) fits well with the published data [3]. The spectrum of sonochemical colloids exhibits the similar characteristic peaks as a hydrolyzed one. On the other hand, the spectrum of sonochemical colloids demonstrates strong Mie scattering which can be related to bigger particles compared to hydrolyzed colloids.

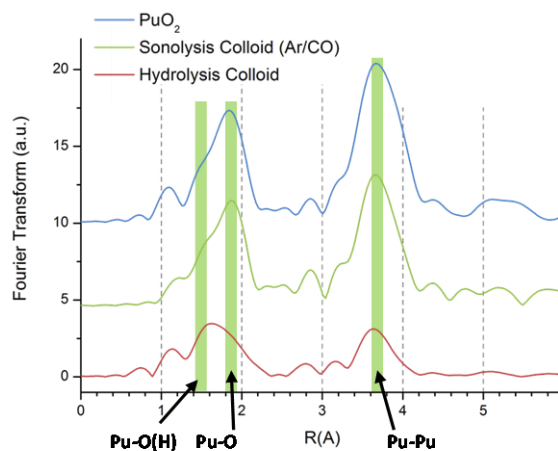


Fig. 2. Fourier transforms uncorrected on the phase shift of Pu L3-edge k^3 EXAFS spectra for sonochemical and hydrolyzed Pu colloids in comparison with PuO_2 calcined at 600°C .

The edge and white line position in Pu L3 XANES spectra show unequivocally the presence of Pu(IV) for both colloids. The Fourier transforms of Pu L3-edge k^3 EXAFS spectra are shown in Fig. 2. The EXAFS spectrum of Pu colloids prepared via sonochemistry reveals Pu-O and Pu-Pu distances quite similar to those in PuO_2 [10] indicating the resemblance of their structures. By contrast, the EXAFS spectrum of colloids obtained by Pu(IV) hydrolysis demonstrates the strong contribution of shorter Pu-O distances attributed to Pu-OH bonds. Moreover, smaller contribution of Pu-Pu bonds in the spectrum of hydrolyzed colloids may indicate a higher structural disorder of these species compared to sonochemical Pu colloids.

The on-resonance absorption contrast STXM images reveal that sonochemical Pu(IV) colloids are composed of nearly monodispersed nanoparticles with the average size less than 20 nm.

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